DEVELOPMENT OF SERIES EMITTANCE THERMAL CONTROL COATINGS

by

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for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

FOREWORD

This document, "Development of Series Emittance Thermal Control Coatings", is the final report on the program conducted during the period of September 1968 to June 1969 for the National Aeronautics and Space Administration under Contract NAS1-8603. The program was monitored by Wayne Slemp of the Langley Research Center of that agency. Mr. B. Linder of the Space Sciences Laboratory, General Electric Space Division, was the principal investigator.

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I. SUMMARY

The purpose of this program was to study the behavior of some candidate series emittance coating materials on exposure in vacuum to ultraviolet light and x-ray or low energy proton radiation. The term "series emittance thermal control coatings" denotes a type of flexible second-surface mirror which utilizes a transparent dielectric film over a reflecting substrate where the thickness of the polymeric film can be varied to obtain a series of coatings with varying α_s/ϵ_T ratios. The materials evaluated included Teflon FEP, poly(vinyl butyral), polyethylene (specially prepared), polycarbonate, poly(vinyl fluoride), and an ultrapure silicone. The experimental procedure involved irradiation in vacuum of unmetallized films and periodic measurement "in situ," i.e., without removal from the vacuum, of the absorption spectrum.

Teflon FEP proved to be the most stable material tested. Poly(vinyl butyral) became more transparent during ultraviolet irradiation, but less transparent during proton irradiation. Polyethylene and poly (vinyl fluoride) were relatively stable to ultraviolet radiation but the latter degraded markedly when exposed to x-radiation. Polycarbonate and ultrapure silicone resin (DC 93-500) degraded rapidly on ultraviolet irradiation.

This study established that the use of the spectral transmission measurements in the .2 to .5 micron wavelength region is an extremely sensitive and reliable method of determining stability of polymeric materials.

II. DISCUSSION

A. Background

Thermal control coatings with "tailored" radiative properties have been used extensively in the aerospace industry to maintain a predetermined heat balance on space vehicles. The tailoring of coatings has been accomplished mainly by the blending of black and white paints to some predetermined proportion resulting in a coating having a solar absorptance (a_s) of between 0.2 and 1.0, and an emittance of 0.70 or higher. While this approach has been moderately successful, it is apparent that the lack of photolytic stability exhibited by these coating systems significantly limits their utility on extended missions.

An alternate approach to providing tailored radiative properties is the "series emittance" concept. This coating system essentially consists of a reflecting metal behind a transparent dielectric film such that the solar absorptance is governed by the metal and the emittance by the thickness of the dielectric film, the emittance increasing with increasing film thickness. These coatings are probably most conveniently used in the form of a tape which is bonded onto the surface of the vehicle. The tape can either be prepared by vacuum metallizing one surface of a polymeric film such as Teflon or by spraying a coating, such as Butvar, onto a thin metal foil. In either case, a pressure-sensitive adhesive would be applied to the metal surface of the tape to permit subsequent bonding to the structure.

The approach has some very distinct advantages over the pigmented surfaces currently being used. The ability to select a level of emittance provides the thermal design engineer with a valuable tool in optimizing the thermal design. The ease with which repair can be accomplished, even up to the launch phase, is also a significant advantage. The most significant benefit, of course, is the photolytic stability which can be imparted to the system by proper selection of materials.

The elimination of pigments has a two-fold effect in providing stability. One, the pigment itself must be stable in order for the coating to be stable. Secondly, the possibility of absorbing ultraviolent radiation with sufficient energy to cause photolytic degradation in the binder of a pigmented coating is greatly increased due to the increased path length which results from the internal scattering of light by the pigment. The series emittance coatings, using a stable metallic reflector instead of crystalline pigments, are more stable than pigmented coatings.

The major drawbacks to utilizing this type of coating for spacecraft thermal control have been the lack of experimental verification of the hypothesized stability of these polymeric materials, and the lack of complete system definition in terms of making and applying the finished tape. The program described in this report deals almost exclusively with eliminating the first drawback in providing data on the stability of these surfaces in a radiation environment.

Certain commercially available materials and test apparatus are identified in this report to specify adequately the materials and apparatus employed. In no case does this identification constitute an endorsement of these products by the National Aeronautics and Space Administration or the General Electric Company.

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B. Experimental

1. Approach

The primary objective of this study was to establish the stability of series emittance thermal control coating materials in a simulated space environment. The degradation of this type of coating as manifested by an increase in solar absorptance is caused, almost entirely, by a decrease in transmission of the polymeric film. The extent of increase in solar absorptance, however, is a strong function of the particular metal utilized as a reflector behind the film.

The technique selected to evaluate the stability of the films was therefore designed to eliminate the contribution of the metal and determine only the change in transmission as a function of exposure. This provides a very sensitive measure of degradation in that it is possible to extend the measurement of transmission down to 0.2 microns. This extension below 0.25 microns (the normal integrating sphere limit), while not significant in terms of solar absorptance calculations, is extremely important in evaluating radiation damage to polymeric materials. The degradation almost invariably begins by a significant increase in absorption in the 0.2 to 0.3 micron region. The fact that photolytic instability manifests itself by increased absorption in this spectral region makes it possible to predict basic instability with a very short testing period, compared to that required if one were examining only the longer wavelength region.

Another benefit derived from making transmission measurements of the film itself is that it is then relatively simple to combine analytically the transmission data with the known reflectance of different metals and calculate the solar absorptance for a particular polymer over different metals. This significantly reduces the number of experiments that need be conducted, since it is conceivable that one would want to use a particular polymer over any one of a half dozen metals. Evaluating each composite would be a time-consuming and expensive procedure.

2. Calculation of Solar Absorptance

The stability of the polymeric films is, as has been stated, best determined by measuring the transmission in the ultraviolet region of the spectrum. The property, however, that is of concern to the thermal design engineer is not the ultraviolet transmission but the solar absorptance. The solar absorptance is a function of the transmission in the 0.2 to 2.0 micron region, the reflectance of the metal, and the front surface reflectance of the polymeric film. A computer program was written for this purpose which computes the spectral reflectance of the composite and integrates over the solar spectrum to compute the solar absorptance from measured spectral transmission, spectral reflectance of the metal and the index of refraction of the polymer.

The program basically solves equation (1) at wavelength intervals corresponding to two percent of the solar energy and computes solar absorptance.

$$RHO_\lambda = Rm_\lambda \cdot e^{\frac{-2k_\lambda c}{\lambda}} - R_{fs} \cdot Rm_\lambda \cdot e^{\frac{-2k_\lambda c}{\lambda}} + R_{fs} \qquad (1)$$

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where RHO_λ = composite reflectance at λ

Rm_λ = metal reflectance at λ

$k_\lambda c$ = extinction coefficient · concentration = - ln [transmission/$(1 - R_{fs})^2$]

R_{fs} = front surface reflectance = $(n - 1)^2/(n + 1)^2$

n = index of refraction of the polymer

λ = wavelength, microns

## 3. Apparatus Description and Experimental Procedure

a. *Irradiation System*

The vacuum system consists of a 12 in. diameter metal bell jar with an adsorption fore-pump and a triode ion pump. It normally operates at about 1×10^{-8} torr without bakeout. The sample was located near the center of the chamber at the focal point of two beams, one ultraviolet and one ionizing radiation.

The ultraviolet source was a high pressure xenon lamp powered by a constant current power supply. The radiation was filtered through 5 cm of Harleco "ultra-pure" water to remove light of wavelengths longer than 0.9 microns. It entered the vacuum chamber through a sapphire window. Intensity measurements were made with a calibrated copper-constantan thermopile and the lamp adjusted to a three sun intensity for almost all the experiments conducted.

X-rays were supplied by a modified XRD-6 generator operated at 3.0 ma and 43 kv. The x-ray intensity at the sample position was determined to be 1.2×10^5 rads/hr by utilizing dye dosimetry curves published by Henley and Richman (Ref. 1).

The proton source was an ORTEC Model 322 RF ion source with Model 335 gap lens and associated electronics. The proton beam intensity was measured to be 0.9×10^{15} protons/cm^2-hr $(2.5 \times 10^{11}$ p/cm^2 - sec) which is considerably higher than the dose rate expected in space. The proton beam was also extremely well focused and at the sample position was only 0.5 cm in diameter. Both the high flux and the small beam diameter were undesirable for the proposed simulation, but it was not possible within the time allotted to modify the geometry sufficiently to reduce the flux and diffuse the beam.

Figure 1 is a schematic representation of the series emittance irradiation apparatus showing the "irradiation" and "analysis" positions of the sample, various irradiation paths, and the in situ transmission measurement path. The sample is mounted on a "flag-like" frame, Figure 2, which is rotated externally by a magnetic feed-through. The sample is held tightly against a water-cooled copper black during irradiation. The geometry of the chamber is such that different areas of the sample received different combinations of radiation, though the analysis light passes only through one horizontal plane, at the position of the proton beam.

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SPECTROMETER
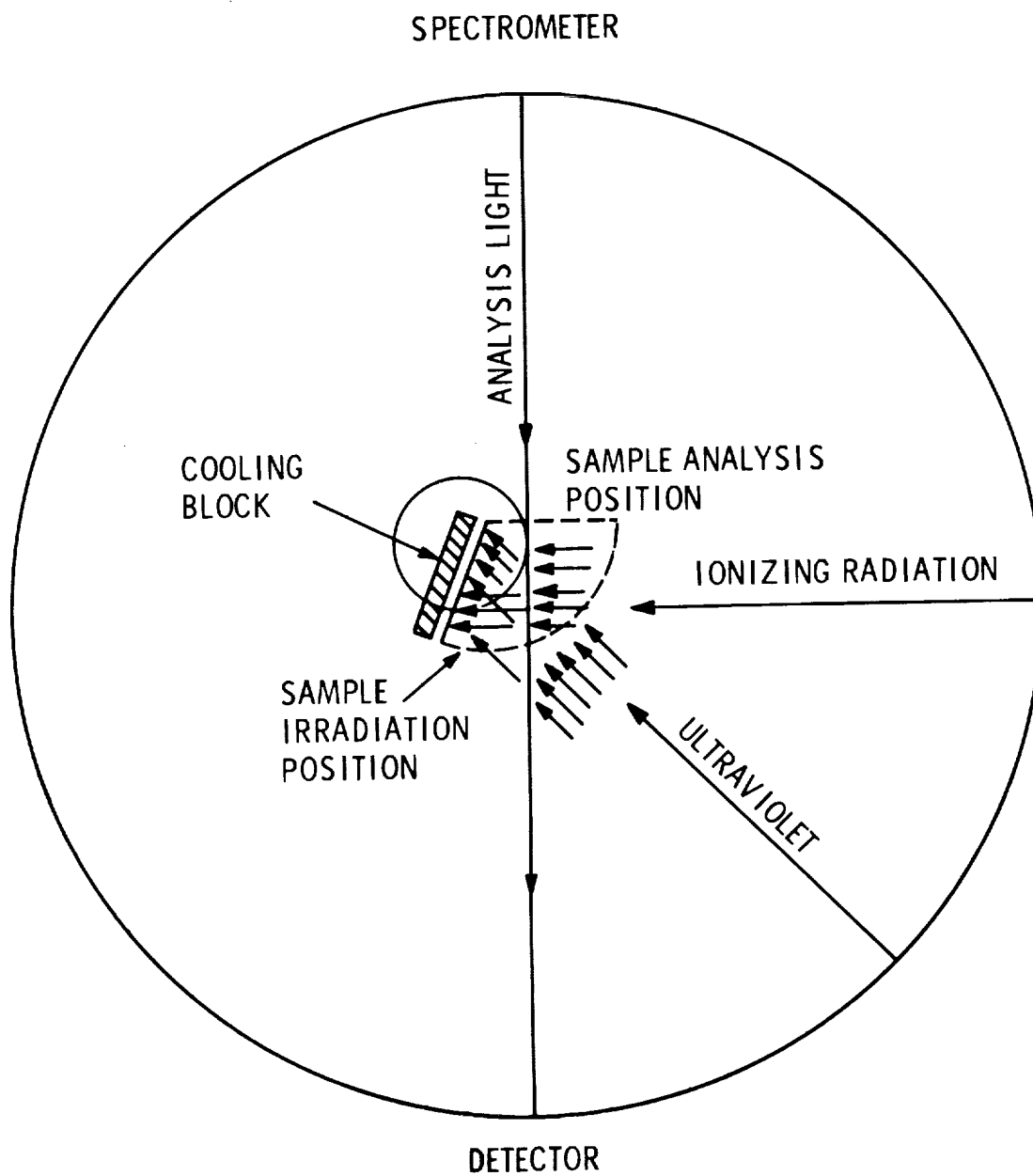
Figure 1. *Schematic of Series Emittance Irradiation Apparatus*

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UV ONLY   UV + X-RAY   X-RAY ONLY

PROTONS

$1\frac{3}{4}$

2"
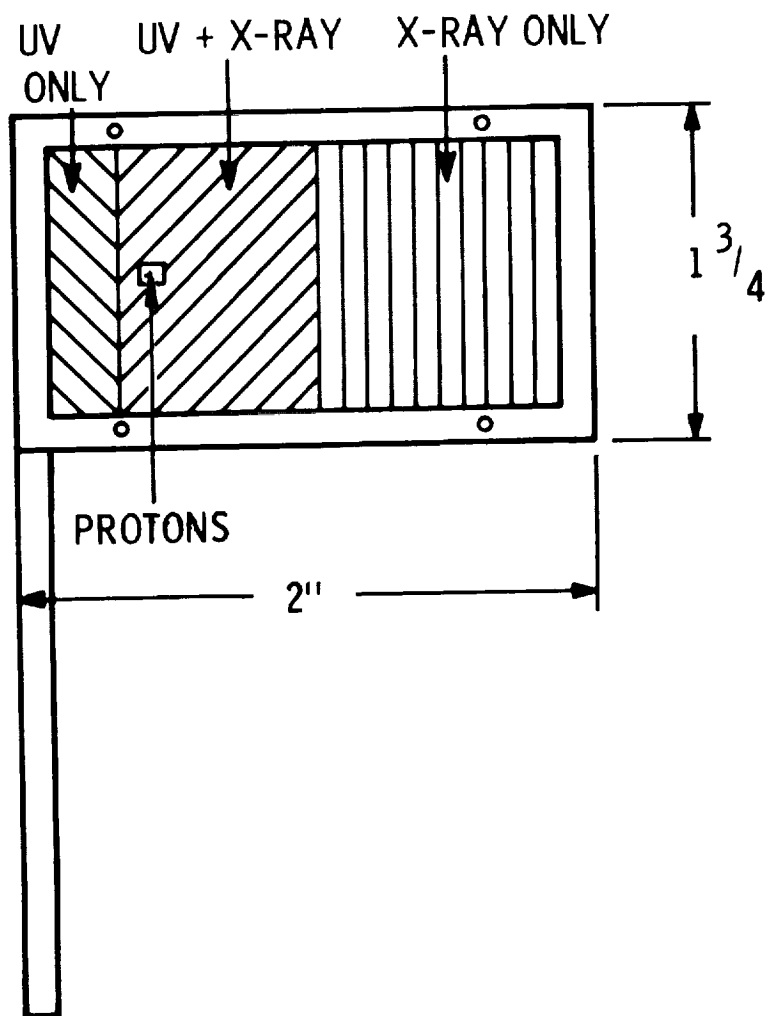
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Figure 2.   Sample Holder

b.   *In Situ Measurement System*

The in situ measurement system consisted of a single beam Perkin Elmer Model 98 monochromator equipped with both hydrogen and tungsten lamps. The light, after leaving the monochromator, passes through a sapphire window into the chamber and out another sapphire window, against which is mounted a suitable detector.

Spectral transmission was determined by making point-by-point measurements. The sample was rotated out of the beam to establish 100% reference and swung into the light to measure transmission at each wavelength. The detectors used were an RCA photomultiplier #7200, which covered the spectral range from 0.2 to 0.65 microns, and a photovoltaic germanium detector for the longer wavelength region. This latter detector did not work adequately and the in situ data are, therefore, reported only out to 0.65 microns. Longer wavelength transmission measurements, however, were made in air before and after exposure utilizing a spectrophotometer with an absolute measuring integrating sphere attachment.

c.   *Experimental Procedure*

The transmission of each sample was measured over the solar spectrum on the Bausch and Lomb Spectronic 505 and/or the Gier Dunkle integrating sphere prior to installation in the irradiation chamber. Infrared transmission was also determined before and after exposure on the Perkin Elmer 421 dual beam spectrometer.

After installation of the sample and evacuation of the chamber, an in situ transmission measurement was made. A comparison between the in situ data and that recorded on the Bausch & Lomb spectrometer is shown in Figure 3. More than thirty spectral transmission data points were recorded between 0.2 and 0.65 microns for each in situ measurement. The time interval between measurements depended to a large extent on the rate of change of transmission but generally determinations were made every 24 hours. After exposure, measurements were again made on the double beam spectrophotometers, of necessity being conducted in air.

The program was started by conducting a screening evaluation of all six polymers, exposing them to either ultraviolet light only and/or to a combined ultraviolet/x-ray flux. The three polymers which were found to be the most stable were then selected for final evaluation in a combined proton/ultraviolet exposure.

4.   **Material Selection**

The principal materials problem associated with series emittance coatings is the choice of polymeric film. The criteria for selecting materials for evaluation on this program were that they be essentially transparent in the 0.3 to 2.0 micron region and be either commercially available or readily formed into free-standing films.

Teflon FEP, Type A — This material was chosen mainly because previous studies (Ref. 2) have show it to be among the most stable polymers in an environment including ultraviolet and ionizing radiation, and because flight experiment data were available to use for comparison with our laboratory simulations.

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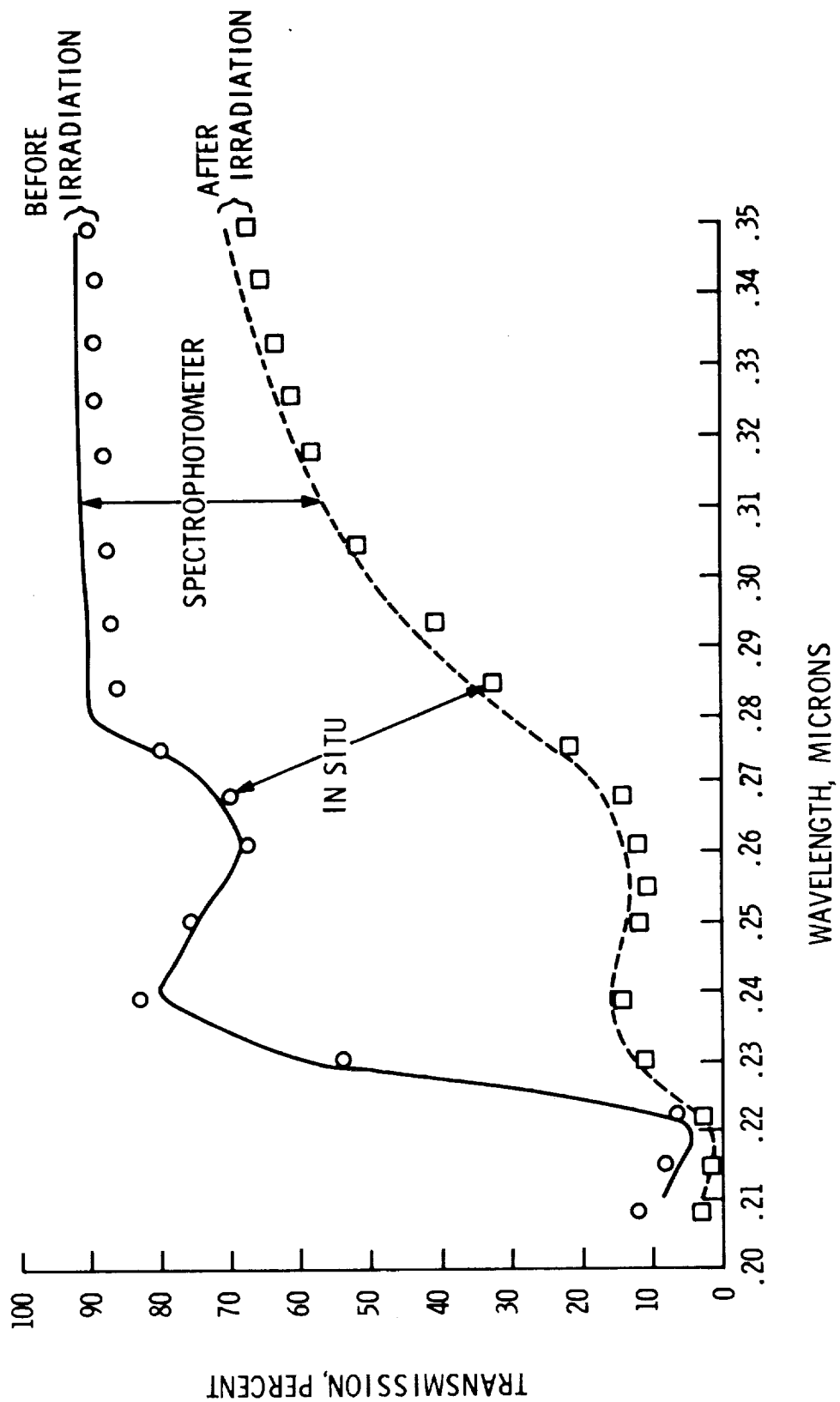
Figure 3. Comparison of In Situ and Spectrophotometer Measurements on Silicon Resin DC 93-500

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Poly(vinyl butyral) — Butvar was a candidate because of its stability as a binder as measured in the phase-change coating study (Ref. 3). It also has the desirable feature of being suitable for spray application either onto a metal foil or directly onto the structure.

Polycarbonate (Kimfoil) — This polymer was selected because it is commercially available as an extremely thin metallized film (less than 0.1 mil) and therefore would be attractive for use where a low emittance is required.

Poly(vinyl fluoride) — The excellent stability of this polymer in sunlight and its structural similarity to Teflon made it appear as a likely candidate especially since it can be more easily formed than FEP.

Polyethylene — This candidate was chosen in the belief that its relatively poor stability to sunlight is not due to the basic polymer structure but due to impurities introduced during the extrusion process which could be easily eliminated and thereby improve stability.

Ultrapure Silicone (DC 93-500) — This polymer was selected for evaluation based upon the expectation that the high purity might improve stability. The material was not a methyl silicone, as expected, but a phenyl silicone which even in the ultrapure state is not stable. It was, however, retained in the screening phase of the program.

5.   Experimental Results

a.   Teflon FEP, Type A

The Teflon film utilized on this study was two mils thick. The initial experiment involved the irradiation with ultraviolet only at an intensity of "one sun" for a period of 350 hours. No measurable decrease in transmission was recorded.

A second sample was exposed to a combined ultraviolet and x-ray flux (UV = 6 ESH/hr., x-ray 1.2×10^5 rads/hr.) for a period of 26 hours. A slight but measurable decrease in transmission was observed at wavelengths shorter than 0.35 microns. No change was observed at longer wavelengths, indicating that only a negligible increase in solar absorptance would result. A graph showing the spectral transmission before and after irradiation is shown in Figure 4.

A third sample was evaluated by irradiating the Teflon film with a combined proton/ultraviolet flux (UV = 3 ESH/hr., protons = $.9 \times 10^{15}$ protons/cm^{2}hr. at 3 kev). Since the proton flux is so much greater than would be expected in space, in situ measurements were made at very short time intervals. Figure 5 is a graphical presentation of the transmission at 8 intervals during 33 hours of irradiation. It is apparent from these data that the damage manifests itself as a decrease in transmission that is not wavelength-dependent. The resultant change in solar absorptance assuming either a silver or aluminum backing is shown in Table I.
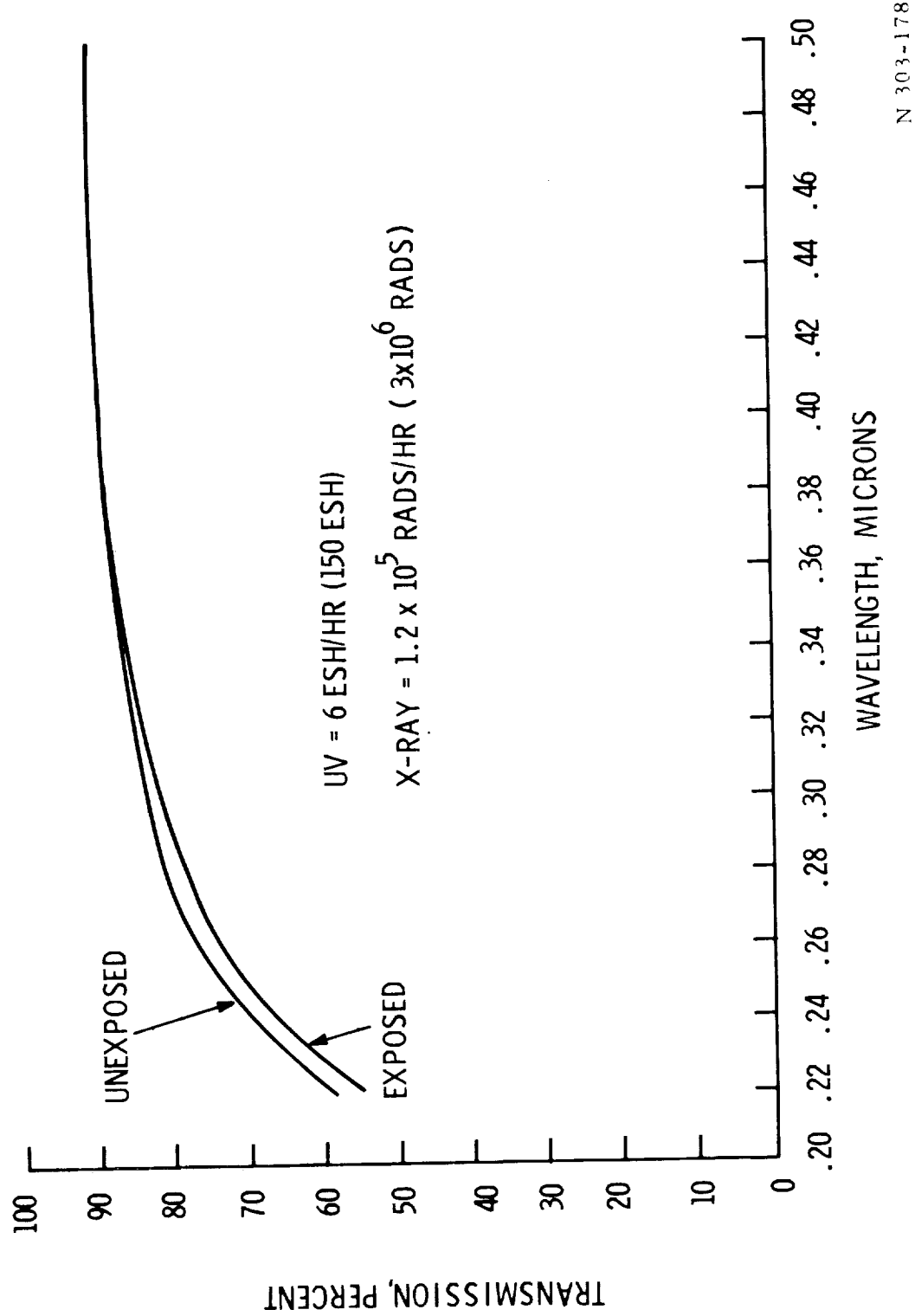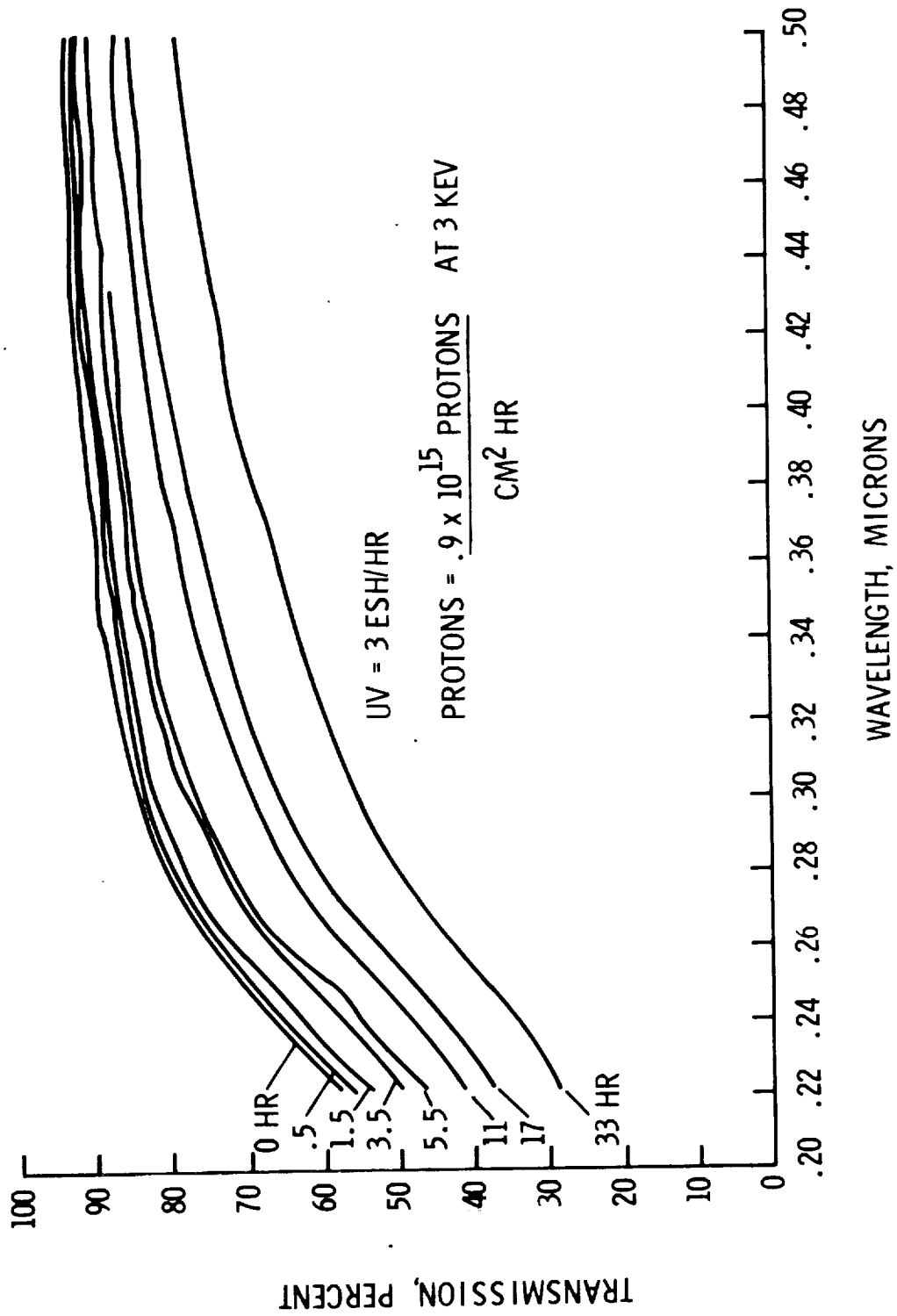
Figure 4. Transmission of Teflon as a Function of UV and X-Radiation

Figure 5.   Transmission of Teflon as a Function of Proton Irradiation

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TABLE I. TEFLON FEP IRRADIATED WITH PROTONS + ULTRAVIOLET

| Duration hrs.	Radiation Dose Ultraviolet ESH	Protons/cm^2 x 10^{-15}	Increase in Solar Absorptance Aluminum*	Silver**
.5	1.5	.45	.010	.011
1.5	4.5	1.4	.017	.018
3.5	10.5	3.2	.029	.031
5.5	16.5	5.0	.035	.037
11.0	33.0	9.9	.059	.061
17.0	51.0	15.0	.070	.077
33.0	100.0	30.0	.13	.13

*   initial α_s = .13
** initial α_s = .051

b.   *Poly(vinyl butyral)*

The Butvar utilized on this program was obtained in powder form from Monsanto Company (manufacturer's designation B98). The films were formed by hot pressing at 400°F and 2800 psi.

The initial experiment was the irradiation with ultraviolet only at 3 ESH/hr. for a period of 83 hours. This resulted in the bleaching of the 0.28 micron absorption band. This significantly decreased the ultraviolet absorption of the polymer and, in principle, increases the subsequent stability (the photon must be absorbed to cause any photolytic degradation). The transmission at selected wavelengths in the ultraviolet is shown plotted against exposure in Figure 6. It is interesting to observe that while the initial rate of bleaching is greatest at the 0.28 micron absorption band, the transmission at shorter wavelengths does not increase significantly until the 0.28 micron band has virtually disappeared. This increased transmission, while extremely important in regard to ultimate stability, obviously has very little effect on solar absorptance in that the percentage of the sun's energy below 0.3 microns (the region most affected) is very small.

The second exposure was a combination of ultraviolet and x-radiation again conducted at 3 ESH/hr. of ultraviolet and 1.2 x 10^5 rads/hr. of x-ray for a duration of 160 hrs. The bleaching of the 0.28 micron band was observed in this experiment as well, but the transmission in this spectral region did not increase as much as in the previous experiment. The ionizing radiation is apparently causing increased absorption and what is ultimately observed is some equilibrium between the
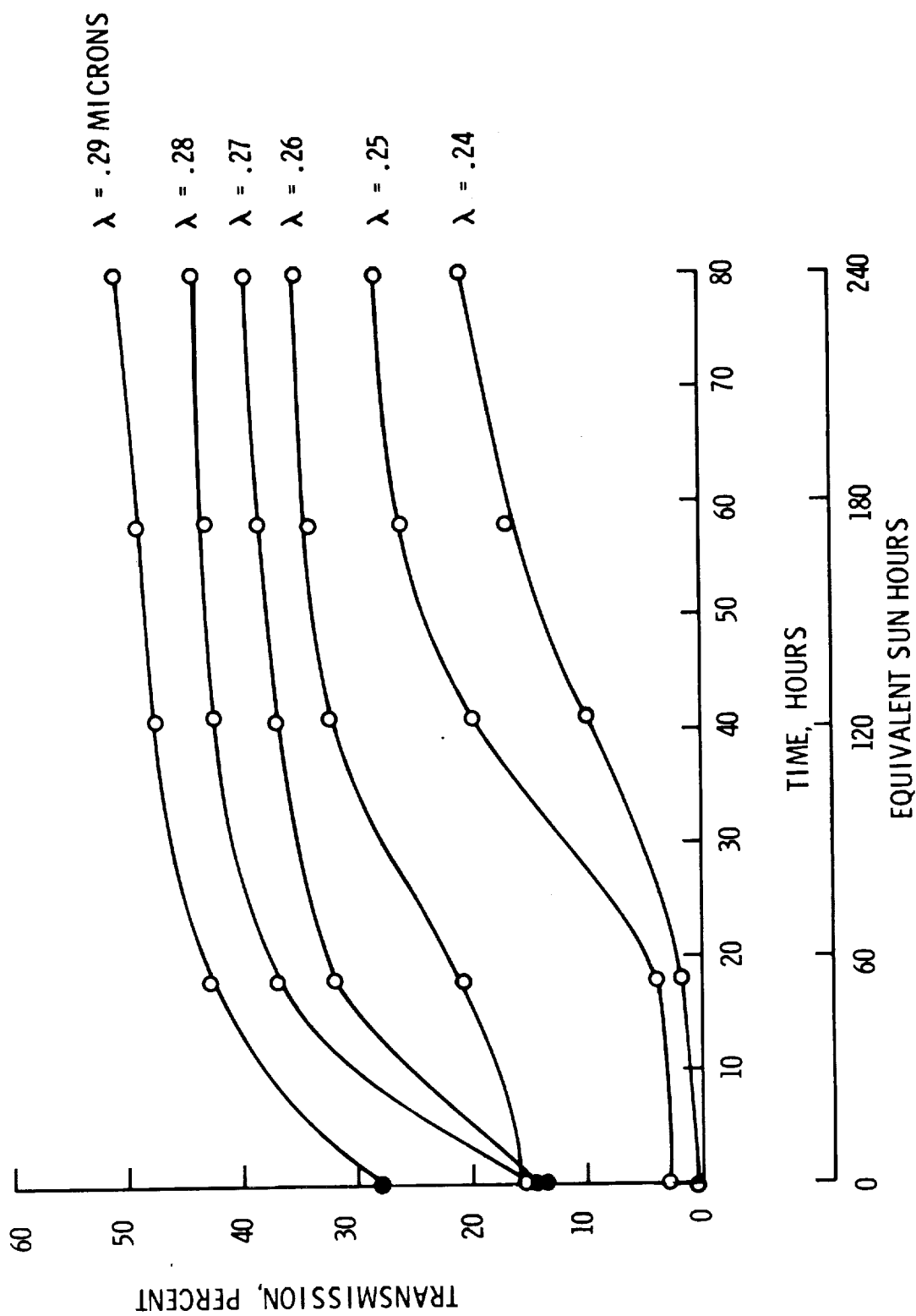
Figure 6.   Ultraviolet Transmission of Poly (Vinyl Butyral)

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competing reactions. Unfortunately, insufficient in situ data are available to calculate the rate constants in each direction, but it appears clear that the ultimate transmission will be a function of the relative intensities of ultraviolet and ionizing radiation. In this case we know we are exposing the sample to a ultraviolet intensity three times as great as will be experienced in space, but do not know how the ionizing radiation rate compares to that encountered in space. A graph showing the spectral transmission of the sample exposed to ultraviolet only and combined ultraviolet + x-ray is shown in Figure 7.

The final experiment conducted with Butvar involved the exposure to a combined ultraviolet and proton flux. The proton flux of 0.9×10^{15} proton/cm^{2}hr., as previously stated, is considerably higher than that expected to be encountered in space. In this case there was no bleaching of the band at 0.28 microns, but a decrease in transmission at wavelengths shorter than 0.32 microns, almost at the start of irradiation. Continued irradiation does not significantly reduce the transmission in the short wavelength region but a large decrease is observed in the longer wavelength region as shown in Figure 8.

The change in solar absorptance due to proton + ultraviolet irradiation is summarized in Table II, assuming a silver or aluminum reflector behind the film.

### TABLE II. BUTVAR IRRADIATED WITH PROTON + ULTRAVIOLET

Duration hrs.	Radiation Dose		Increase in Solar Absorptance	
	Ultraviolet ESH	Protons/cm^2 x 10^{-15}	Aluminum*	Silver**
1	3	0.9	.015	.018
5	15	4.5	.14	.18
23	69	20.7	.24	.31

* initial $\alpha_s = 0.17$
** initial $\alpha_s = 0.14$

c. *Polyethylene*

The polyethylene polymer was obtained from the Celanese Corporation. The material (60-500 flake) was in powder form and differs from the commerically available polymer in that it had never been through the extrusion process. This difference is significant in terms of the ultimate photolytic stability of the polymer, since the extrusion process increases the concentration of carbonyl groups in the polymer chain. An infrared transmission curve of a film made with this polymer compared to a commercially available film clearly shows the difference in carbonyl concentration (decreased absorption at 1750 cm^{-1}).
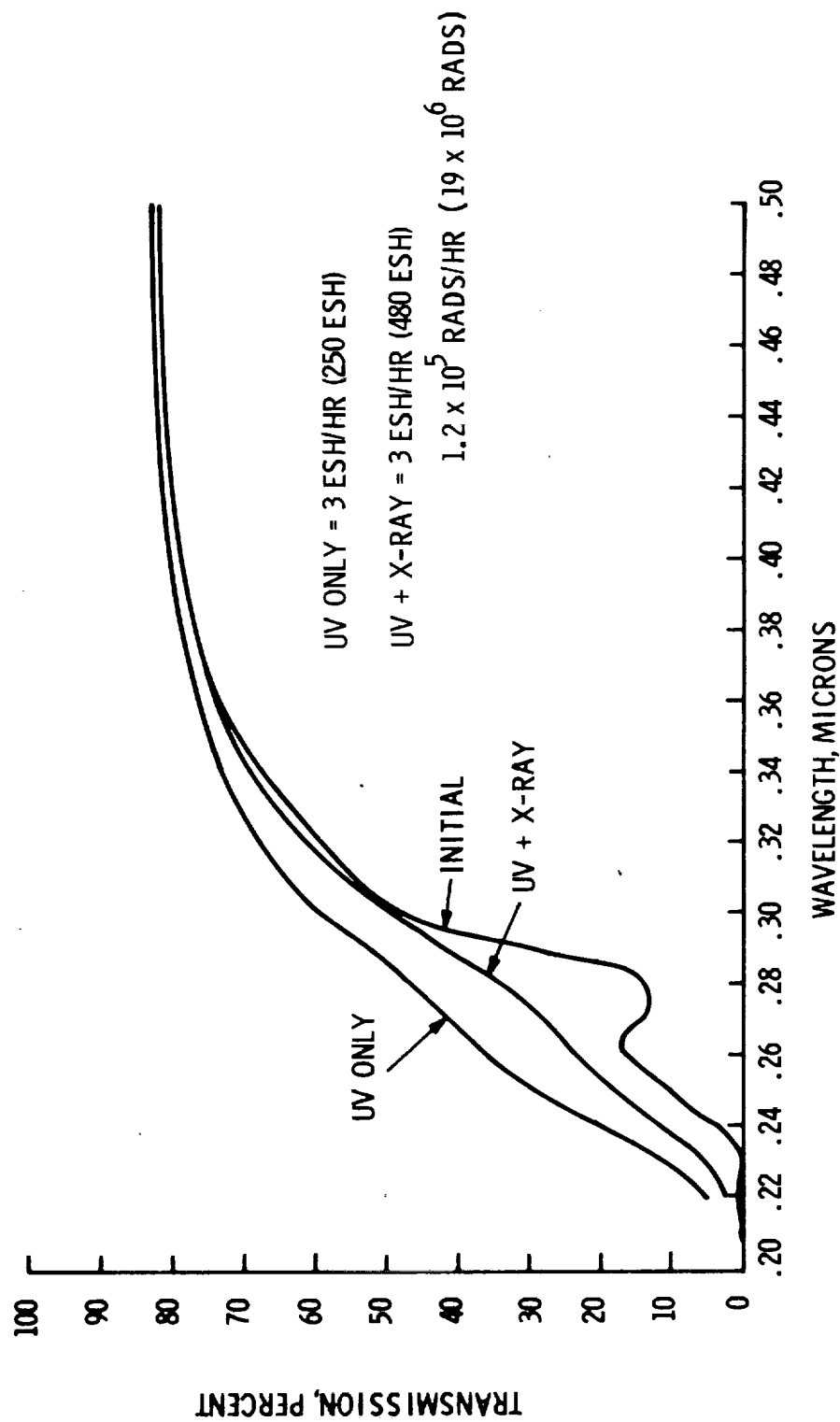
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Figure 7. *Transmission of Poly(vinyl Butyral) as a Function of UV and UV + X-Irradiation*

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UV = 3 ESH/HR

$\text{PROTONS} = \dfrac{.9 \times 10^{15}\ \text{PROTONS}}{\text{CM}^2\ \text{HR}}$ AT 4 KEV

INITIAL

1 HR

5 HRS

23 HRS

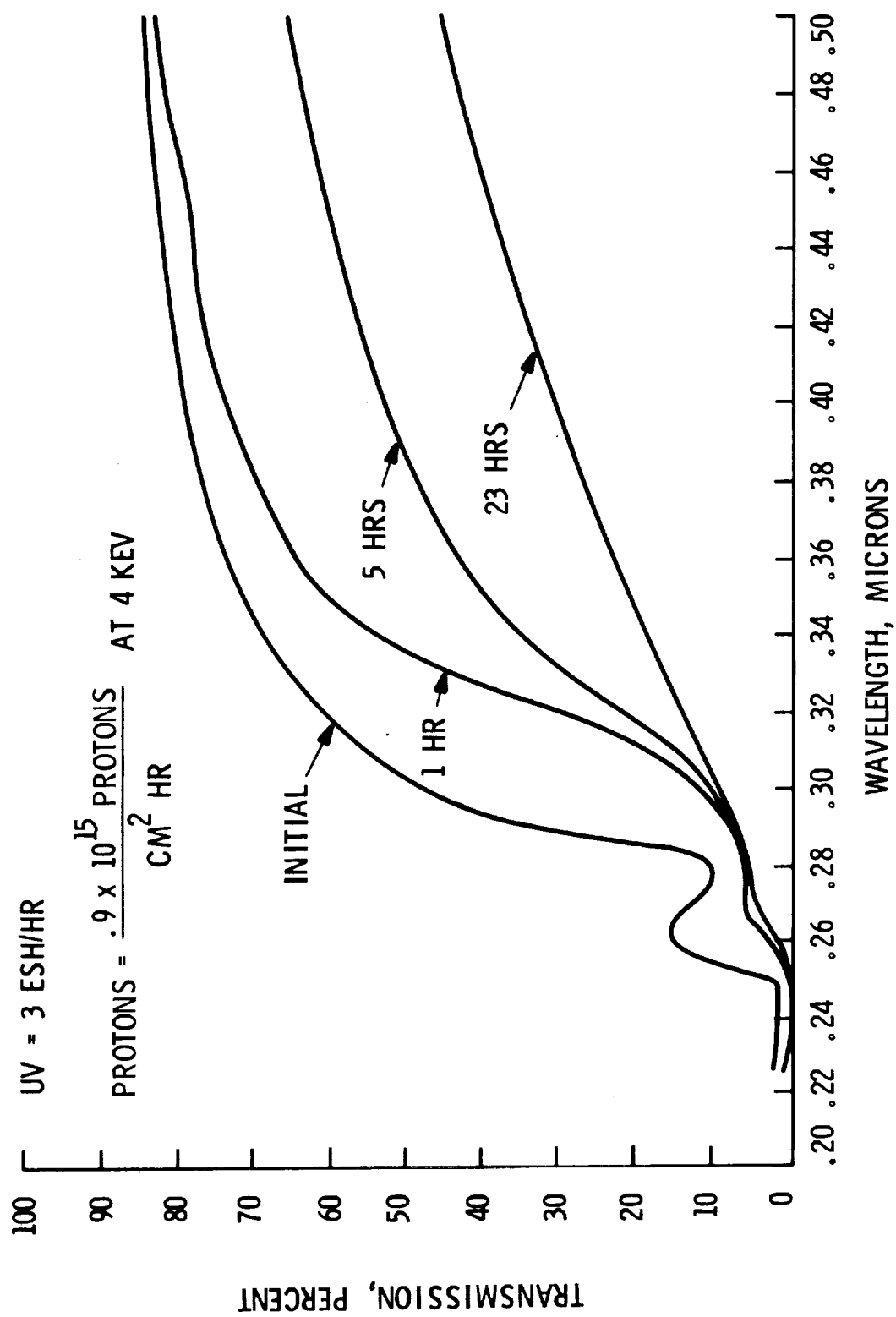TRANSMISSION, PERCENT

WAVELENGTH, MICRONS

Figure 8. Transmission of Poly(vinyl Butyral) as a Function of UV and Proton Irradiation

A major problem encountered in utilizing this material is the difficulty in preparing a truly transparent film. The films utilized were pressed at elevated temperatures but still were not clear. The haziness, resulting from light scattering by crystallites in the film, reduces the specular transmission to levels which make it unacceptable for this application. It appears probable, that should further study of this polymer be warranted, clearer films could be formed by spraying from a heated solvent. There was not sufficient time allotted on this program to pursue this technique.

The lack of clarity in the film is not a major drawback in evaluating the change in absorption due to irradiation, but it does prevent making meaningful predictions of solar absorptance since the computer program does not take into regard light scattering within the film.

Two experiments were conducted with the polyethylene film. The first was exposure to ultraviolet radiation only, the result of which is shown in Figure 9. There is a decrease in transmission of a few percent which shows no spectral selectivity. It is possible that even this small change could be further minimized, if the film were clear, in that this would reduce the path length of the photon in the polymer.

The second experiment, involving the irradiation of a somewhat more transparent film, was a test of stability to a combined proton-ultraviolet flux. The behavior, as shown in Figure 10, was similar to that of the Teflon film with a continued decrease in transmission at all wavelengths and essentially no spectral selectivity.

d.   *Poly(vinyl fluoride)*

The poly(vinyl fluoride) was obtained from E. I. DuPont as an extruded film. The polymer was irradiated with ultraviolet only at 3 ESH/hr. for 60 hours and no significant change in transmission was recorded. This same sample while still in the vacuum chamber was then irradiated with x-rays at 1.2×10^5 rads/hr. while continuing the ultraviolet exposure. (This represents a departure from the procedures used for all the other data reported, where a different sample was utilized if the radiation flux was changed.)

The large decrease in transmission resulting from the combined ultraviolet and x-ray exposure is shown in Figure 11. Also shown on this curve, is a transmission spectrum (measured in air after completion of irradiation) of that portion of the film that was irradiated only with x-rays. It is apparent that the damage due to x-ray + ultraviolet exposure is significantly greater than that due to the sum of the two independently. It appears that the ionizing radiation results in the formation of HF, leaving a polymer with conjugated unsaturation (note absorption bands at 0.23, 0.28, 0.32, 0.36 microns) which is more susceptible to damage by ultraviolet radiation than the original polymer. The results of this exposure precluded making any further experiments with poly(vinyl fluoride).

e.   *"Ultrapure" Silicone (DC 93-500)*

The polymer was obtained in liquid form from the Dow Corning and cast into a film for evaluation on this program. As indicated previously, it was initially thought that this material was a
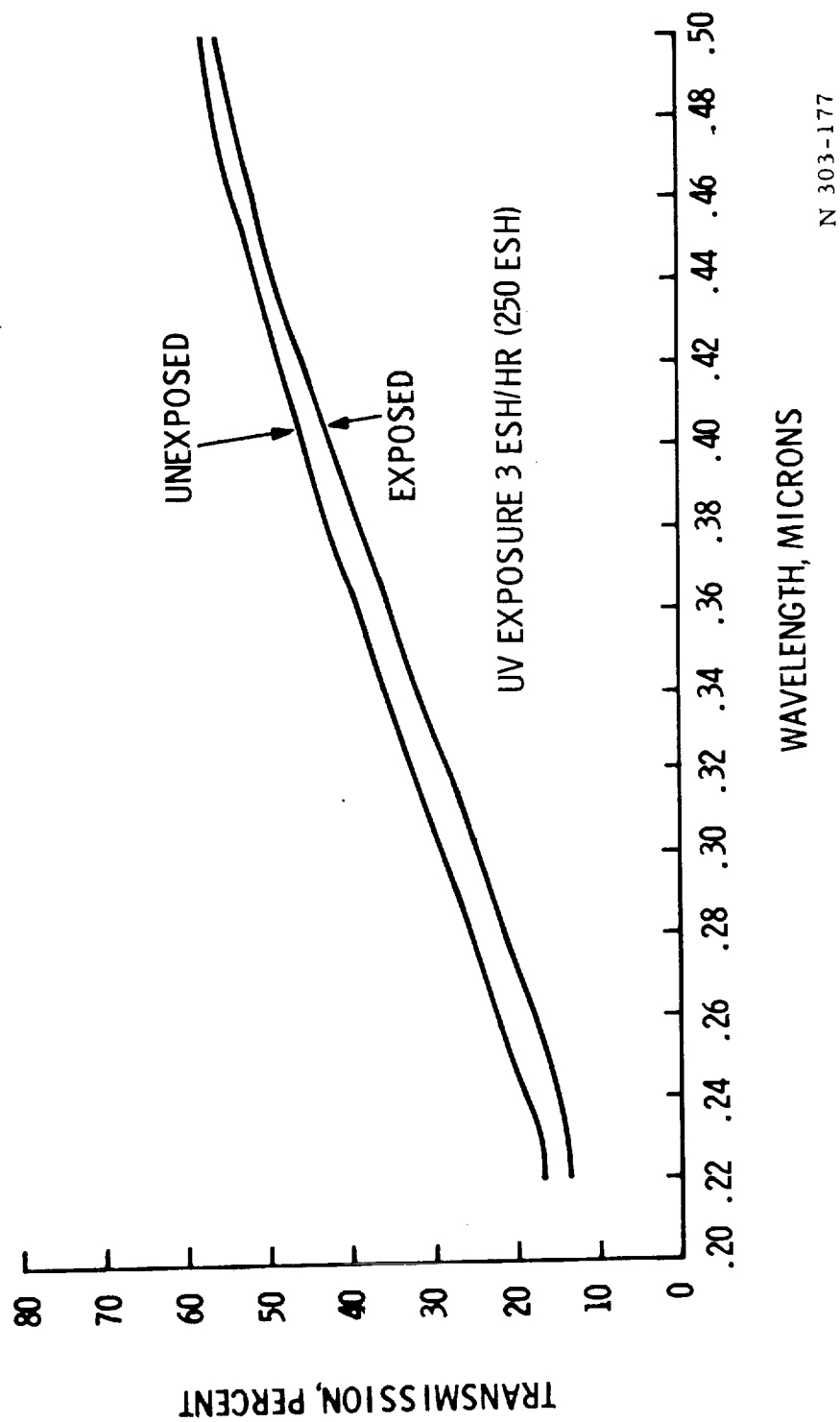
Figure 9. Transmission of Polyethylene as a Function of UV Irradiation

The figure shows a graph with TRANSMISSION, PERCENT on the vertical axis (0 to 80) and WAVELENGTH, MICRONS on the horizontal axis (.20 to .50). Two curves labeled UNEXPOSED and EXPOSED are shown.

UV EXPOSURE 3 ESH/HR (250 ESH)

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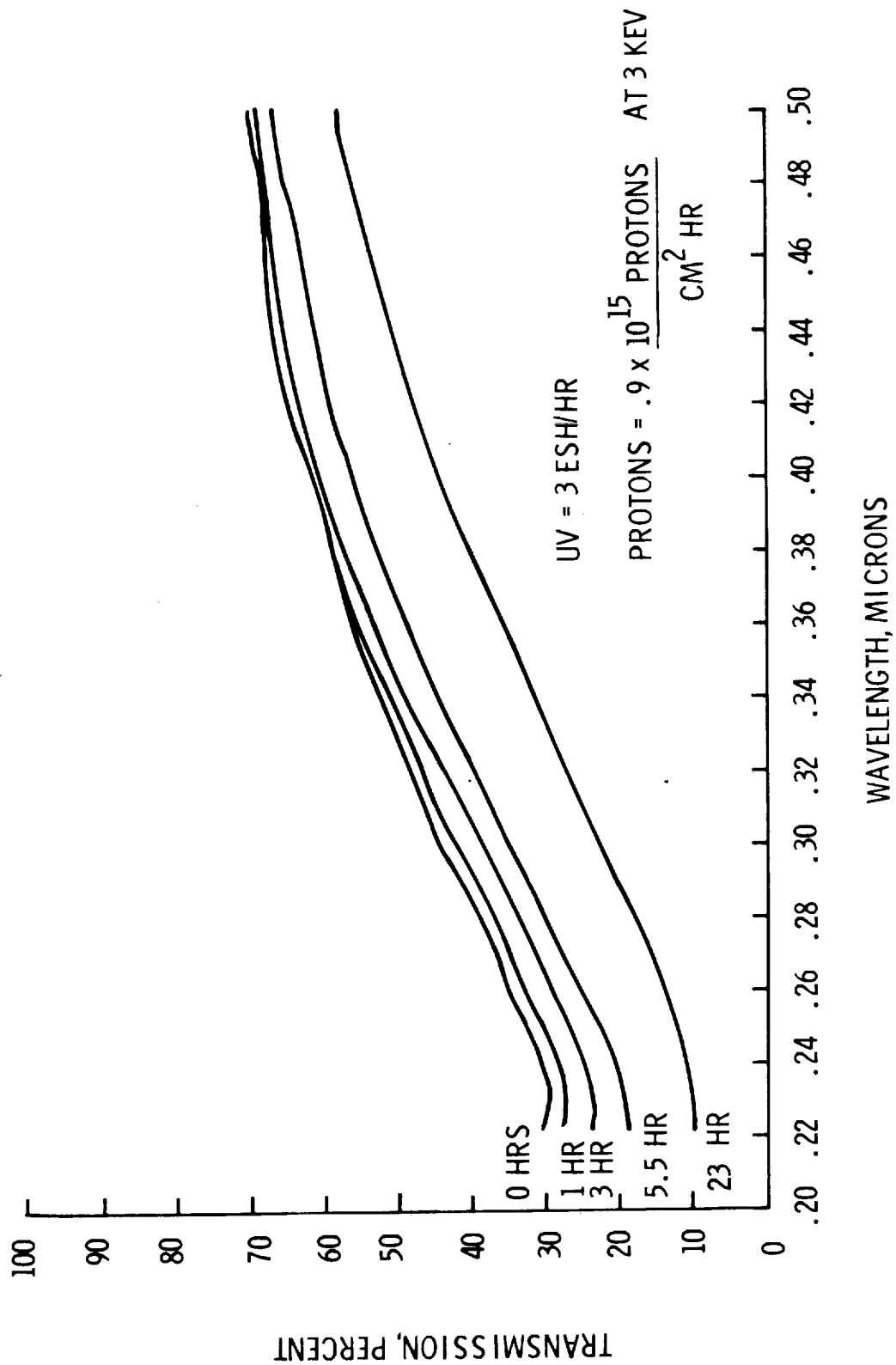
Figure 10. *Transmission of Polyethylene as a Function of UV + Proton Irradiation*
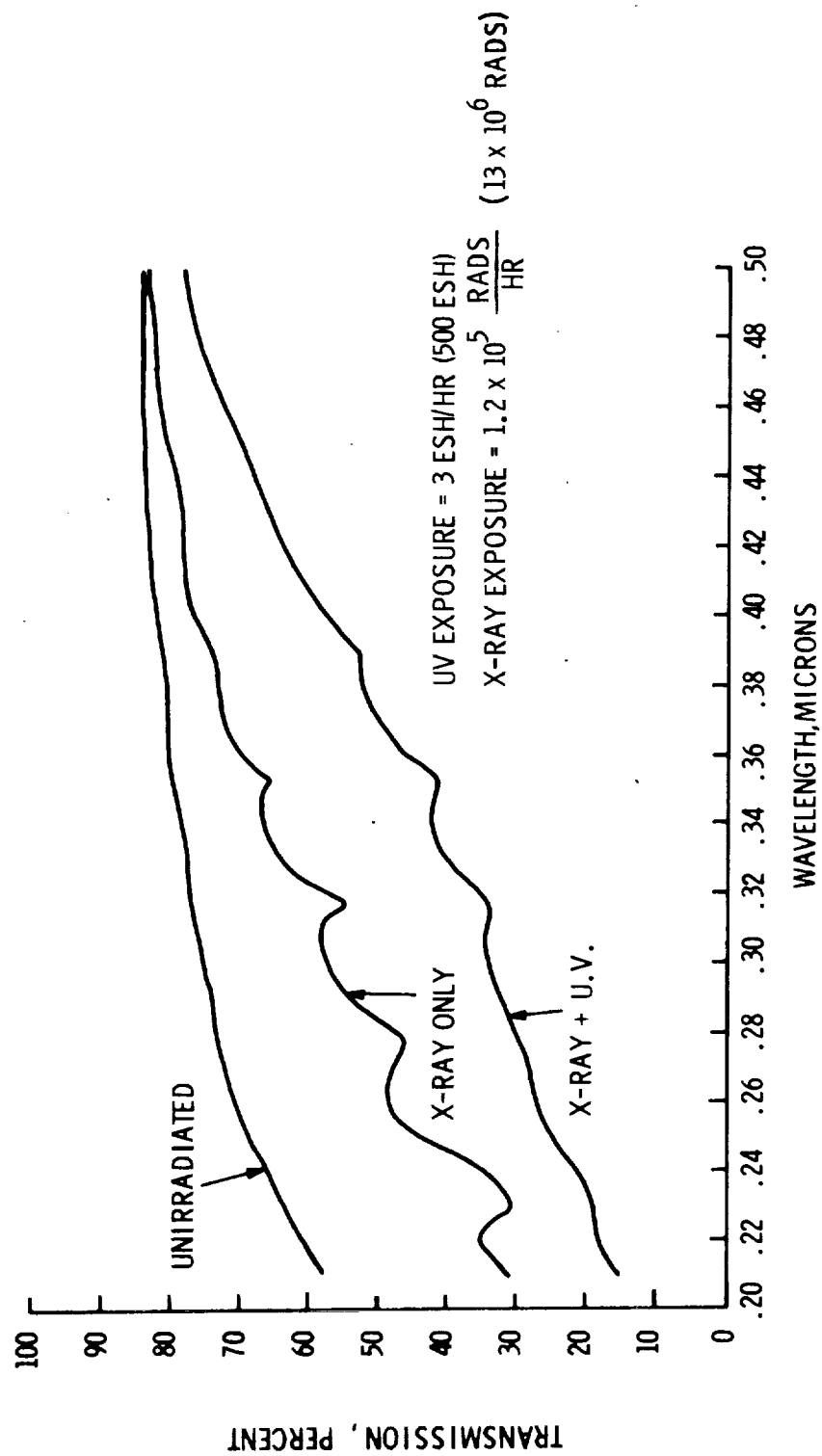
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Figure 11. Transmission of Poly(vinyl Fluoride) as a Function of X-Irradiation and UV + X-Irradiation

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methyl silicone and, having been specially purified, it might make an interesting candidate for this application. As is obvious from the absorption band at 0.26 microns in the initial transmission curve, shown in Figure 12, the material is a phenyl silicone and therefore probably not stable to ultraviolet radiation. The lack of stability is clearly seen in Figure 12 where the transmission is shown as a function of ultraviolet dosage. No further evaluation of this polymer was conducted on this program.
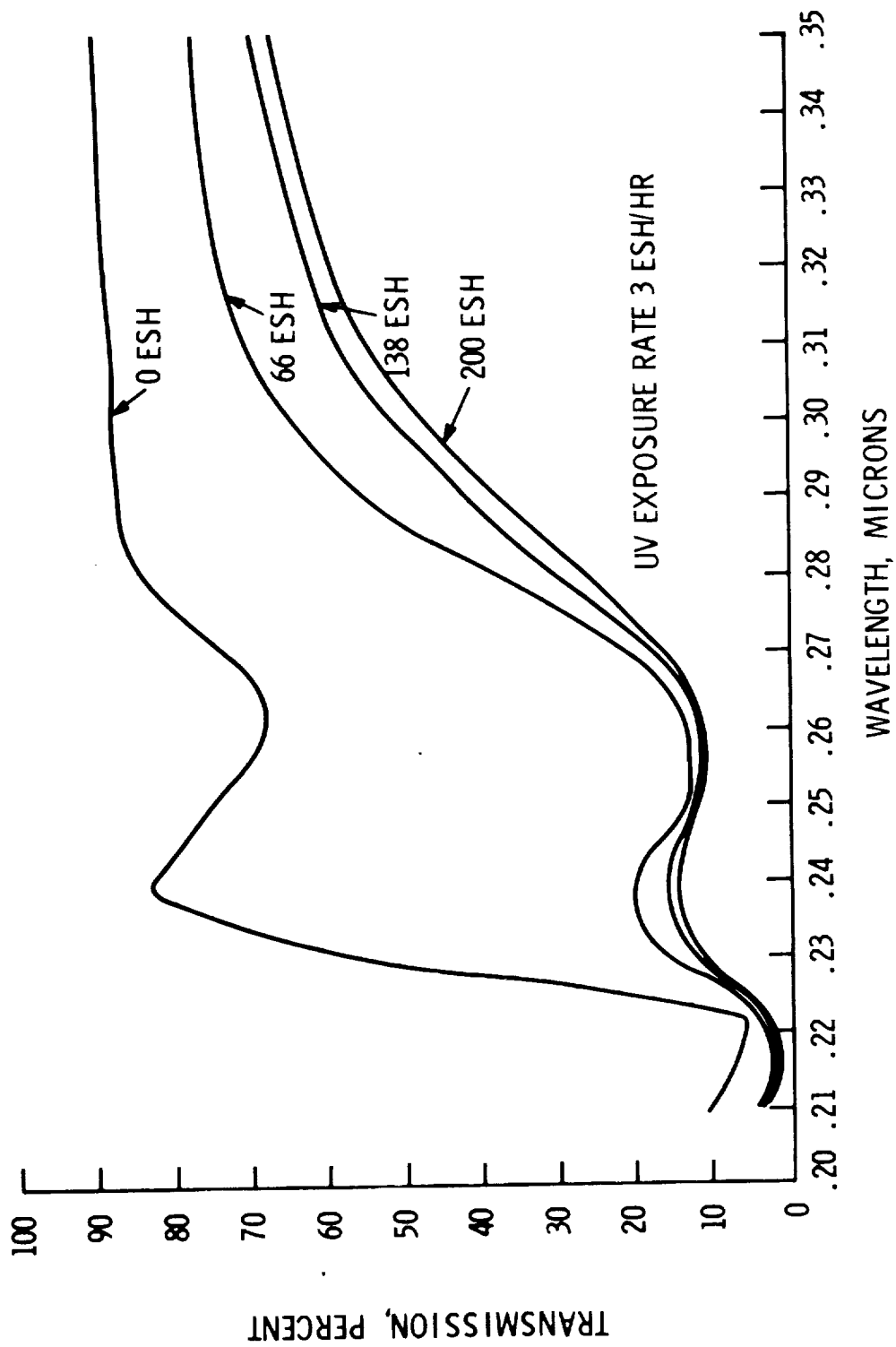
f. *Polycarbonate*

The polycarbonate film was acquired from the Kimberly Clark Corporation as a free-standing unmetallized film. This material is identical to that produced by this company as a metallized film in thicknesses down to 0.08 mils. This polymer, like the polyethylene film, is somewhat hazy and therefore it is not possible to make meaningful predictions of solar absorptance from transmission measurements.

The material was exposed to ultraviolet radiation at 3 ESH/hr. for a period of 70 hrs. and degraded so markedly that no further evaluations were conducted. The transmission of the film before and after exposure is shown in Figure 13.

C. Concluding Remarks

The technique of measuring the in situ spectral transmission of polymeric films down to wavelengths of 0.2 microns has proven to be a useful tool in evaluating their stability in a vacuum radiation environment. Not only is it useful in that photolytic degradation can be detected during its incipient stages, but it provides data which can be analytically paired with any number of different metallic reflectors to allow the calculation of solar absorptance. The technique, in addition to minimizing the number of experiments which must be conducted, can be used to select the optimum reflector for a particular film.

The underlying principle behind the optimization of metal selection is that the reflector should be chosen so that it has a low reflectance in the spectral region where the polymer undergoes a large change in transmission. This is probably best illustrated using as an example a very unstable polymer such as the silicone resin DC 93-500 (transmission data presented in Figure 12). It undergoes a very significant decrease in transmission in the short wavelength region below 0.4 microns which at least for the 200 ESH exposure does not extend significantly beyond 0.5 microns. If a flat reflector such as aluminum (about 0.92 reflectance) is used behind the film, the solar absorptance goes from 0.096 to 0.14 as result of exposure. The utilization of silver in this case does not really help much, because although it minimizes the change in reflectance (ΔR) in the region below 0.32 microns, this is compensated for by the increased ΔR in the longer wavelength region (0.35 to 0.50 microns) where the silver reflectance is about 0.95. The α_s before and after exposure for this combination is 0.067 and 0.099, respectively. A very large improvement, however, is observed if one chooses copper as the reflector, since the reflectance is relatively low below 0.5 microns. The solar absorptance is 0.18 initially and only goes to 0.20 after irradiation. The reflectance curves for silicone resin DC 93-500 before and after irradiation are shown in Figure 14 for each of the three metals discussed.

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Figure 12. Transmission of Silicone Resin DC 93-500 as a Function of UV Irradiation
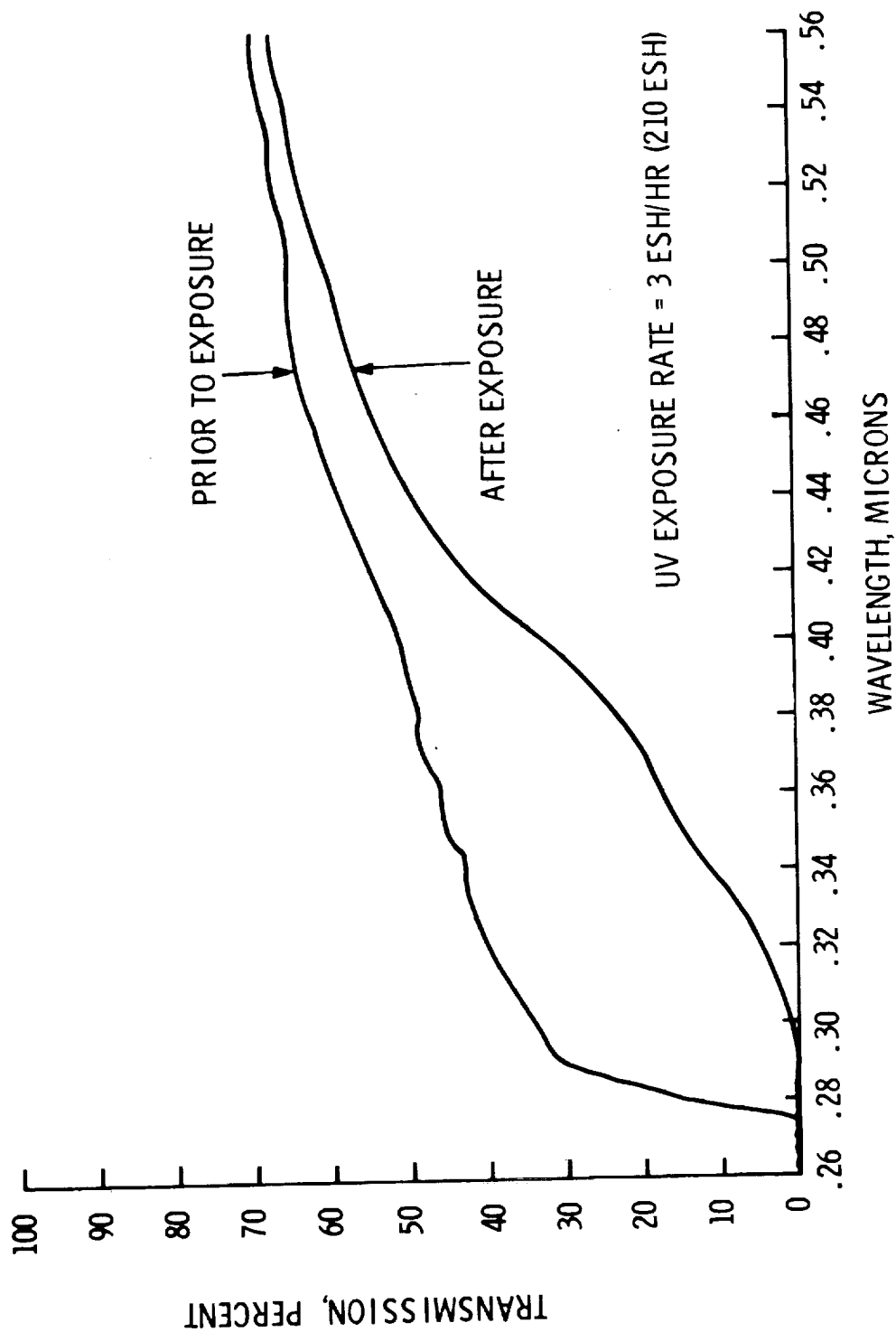
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Figure 13. Transmission of Polycarbonate Film as a Function of UV Irradiation

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METAL REFLECTOR	SYM.	α_s init.	α_s final	% CHANGE	$\Delta\alpha/\alpha$
SILVER	○	.067	.099		.48
ALUMINUM	□	.096	.14		.48
COPPER	△	.18	.20		.11

UV ONLY 200 ESH

DASHED LINES – AFTER EXPOSURE
SOLID LINES – BEFORE EXPOSURE

SILVER
COPPER
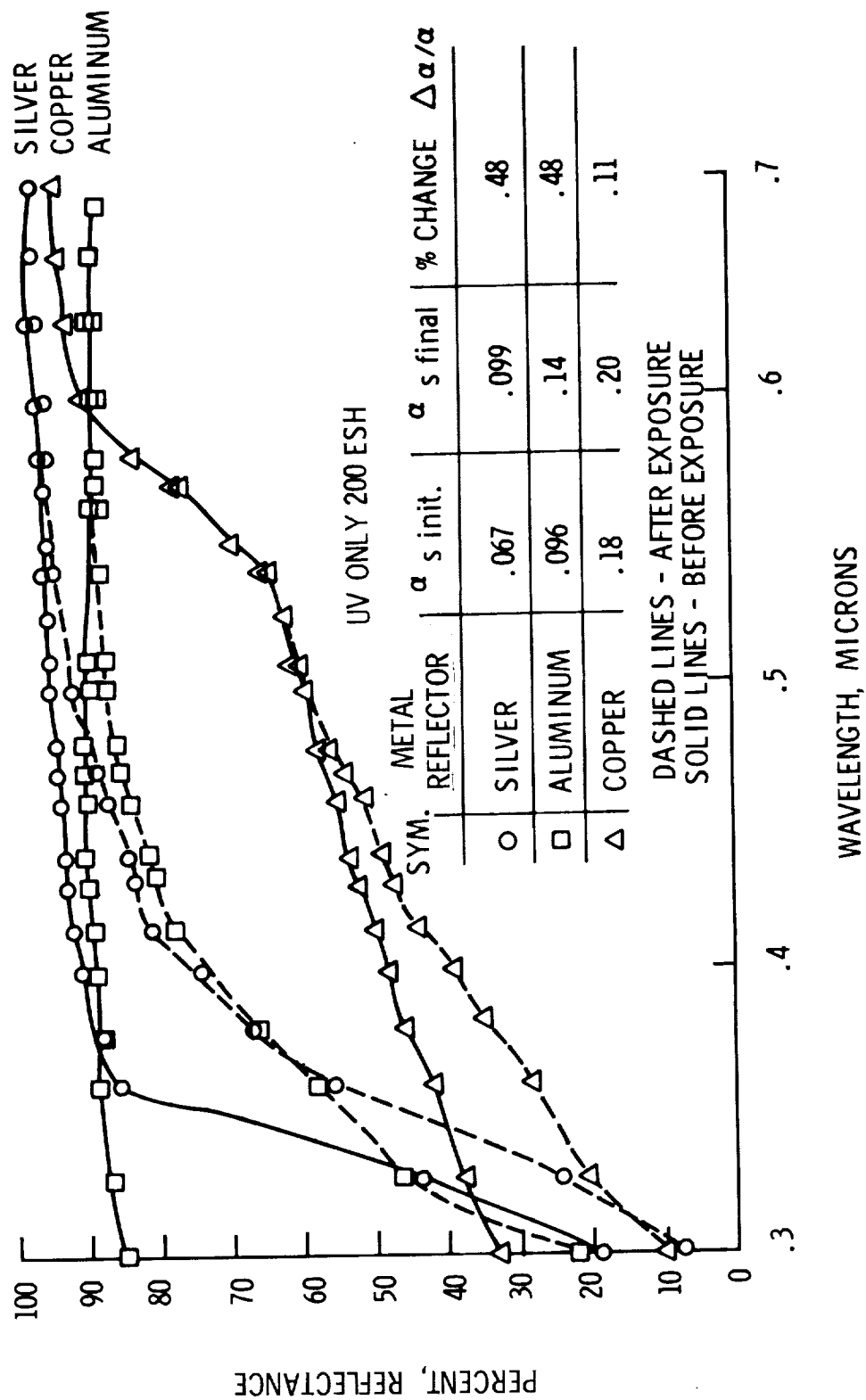ALUMINUM

PERCENT, REFLECTANCE

WAVELENGTH, MICRONS

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Figure 14. Effect of Metal Selection on Reflectance for Silicone Resin DC93-500

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The calculated values of solar absorptance, using the calculation procedure described in section B2, for each of the polymers evaluated, except polyethylene and polycarbonate, are presented in Table III. The values of metal reflectance used are those determined by Hass and reported in Ref. 4. These particular reflectance values were selected for this calculation because they provide a set of data which is self-consistent and therefore is useful for making comparisons. Aluminum reflectance data measured at G.E. is considerably lower than that reported by Hass. It is included because we believe it more closely represents the properties of surfaces that one would obtain in a commercially metallized film.

Examination of Table III indicates that of the six polymers evaluated, only two, Teflon and Butvar, are sufficiently stable to be considered for eventual use as series emittance thermal control coatings. Polyethylene appears to be sufficiently stable to warrant further consideration, but techniques for making more transparent films need to be evolved.

The interpretation of Teflon data is relatively straightforward. There is no measurable decrease in transmission due to ultraviolet for a period of 350 ESH. Since any incipient damage would manifest itself first in the short wavelength ultraviolet region and none has been observed, it appears safe to state that the Teflon film would undergo no significant change in solar absorptance due to ultraviolet irradiation for periods of at least 500 ESH. The stability in the combined ultraviolet/x-ray exposure was not as good, but even in this environment the change is extremely small and has a negligible effect on solar absorptance. The testing at 10^5 rads/hr. was an arbitrary selection and therefore we are in no position to relate this to actual space exposure. It is apparent that the damage is not catastrophic and basically the film is useable for missions where combined ultraviolet and x-radiation impinge on the vehicle.

Proton impingement obviously does degrade the film with a resulting increase in solar absorptance. While this is undoubtedly undesirable, one must consider the rate of increase of solar absorptance in terms of hours in space to ascertain the extent of damage to be expected on any particular mission. This requires an accurate assessment of the proton flux intensity expected to be encountered in space. This data is not readily available but since aluminized Teflon was flown as a flight experiment on Mariner V (Ref. 5), some comparisons can be made. If one assumes a proton flux of 1.5×10^{12} protons/cm²hr. impinging on the vehicle, and that the protons and not the ultraviolet cause the degradation, excellent agreement results between the laboratory and flight data. The solar absorptance as measured on that mission is compared to our laboratory data in Table IV and Figure 15.

The close agreement between the data measured by NASA on the Mariner and our laboratory experiments not only permits making real-time estimates of performance in space but also answers questions regarding accelerated testing. We did not choose to test 600 times as high as what was considered a reasonable simulation but experimental difficulties and lack of time prevented making suitable alterations. At least for Teflon, based on this excellent agreement in data, it appears that accelerated testing may be a valid approach.

The behavior of poly(vinyl butyral) in a combined ultraviolet and ionizing radiation environment is considerably more complex than that of Teflon. The experiment conducted with

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TABLE III. SOLAR ABSORPTANCE CALCULATIONS

Dielectric	Gold	Copper	Silver	Aluminum		Radiation Dose
None	.19*	.17*	.051*	.081*	.12**	
Teflon - 2 mils (no irradiation)	.20	.18	.070	.10	.13	
Teflon - 2 mils (irradiated)	.20	.18	.070	.10	.13 .20	180 ESH + 4 x 10^6 rads x-ray 51 ESH + 1.5 x 1016 protons/cm2 at 3 kev
Poly(vinyl fluoride) - 1 mil (unirradiated)	.22	.20	.097	.13	.16	
Poly(vinyl fluoride) - 1 mil (irradiated)	.25	.23	.14	.18	.21	500 ESH + 13 x 10^6 rads x-ray
DC 93-500 - 3 mils (unirradiated)	.20	.18	.067	.096	.13	
DC 93-500 - 3 mils (irradiated)	.22	.20	.099	.14	.17	200 ESH
Butvar - 8 mils (unirradiated)	.23	.21	.10	.14	.17	
Butvar - 8 mils (irradiated)	.23	.21	.098	.14	.16 .42	250 ESH 70 ESH + 2.1 x 1016 protons/cm2 at 4 kev

*Ref. 4

**Reflectance Data Measured at GE

TABLE IV. COMPARISON OF LABORATORY AND FLIGHT EXPERIMENT DATA
FOR TEFLON

Proton Flux in Space Assumed to be 1.5×10^{12} Protons/cm^2 - hr.

Equivalent Sun Hrs.	Solar Absorptance	
	Mariner*	G.E. Predicted**
0	.130	.132
300		.142
500	.146	
900		.149
1,000	.150	
1,500	.155	
2,000	.162	
2,100		.161
2,500	.167	
3,000	.170	
3,300		.167
3,500	.173	
4,000	.175	
4,500	.177	
5,000	.179	
6,600		.191
10,200		.203

* Ref. 5

**Based on aluminum reflector behind Teflon.
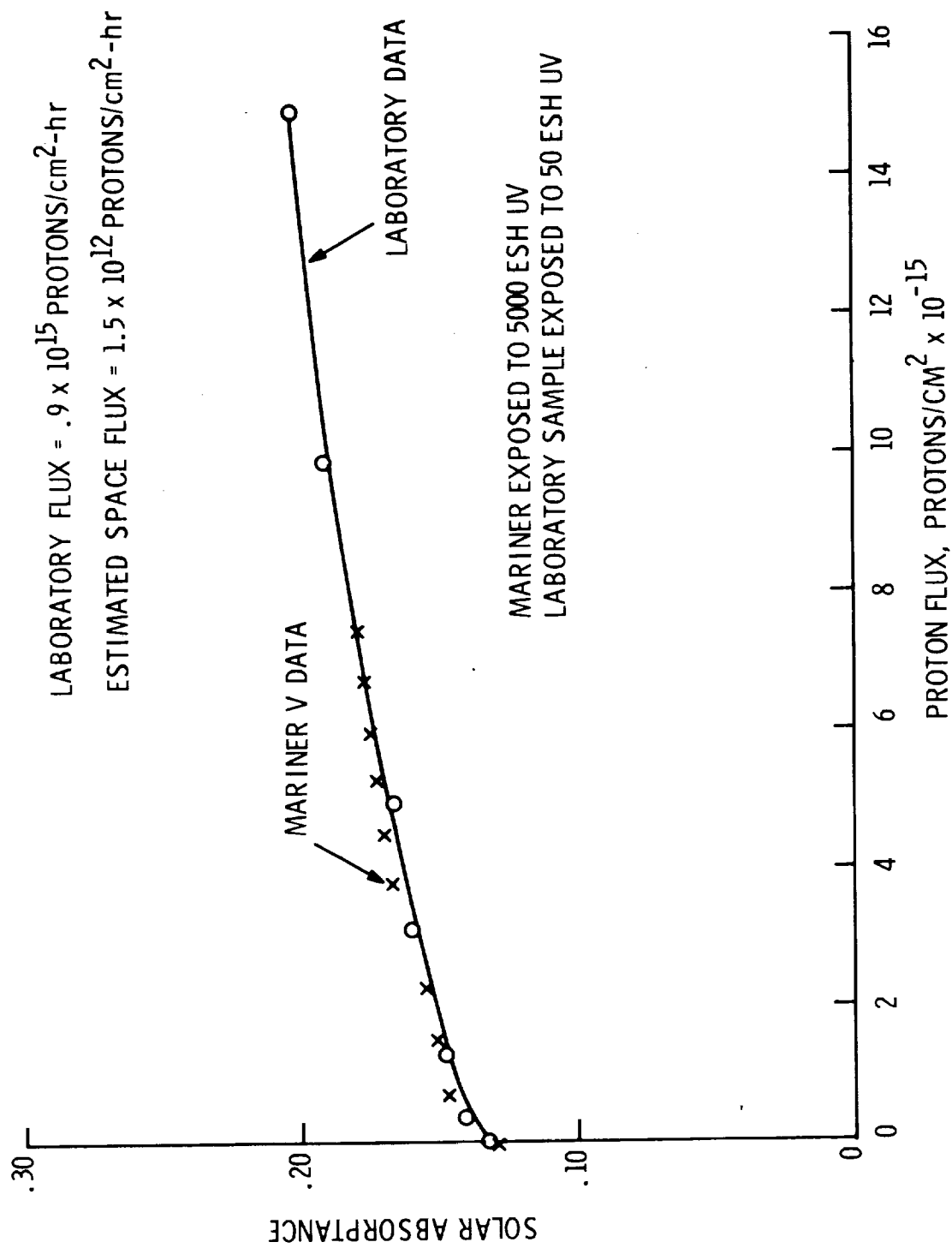
Figure 15. *Comparison of Mariner V Flight Data with Laboratory Data for Aluminized Teflon (Based on Equivalent Proton Flux)*

ultraviolet radiation alone clearly shows the removal of a carbonyl group from the polymer. This is demonstrated not only by an increase in transmission at 0.28 microns, but also by the virtual disappearance of the infrared absorption bands 1630 cm^{-1} and 1680 cm^{-1} due to this group. The removal of the band at 0.28 microns, while having only a negligible effect on solar absorption is now considerably reduced. The exposure to a moderate dose of ionizing radiation in conjunction with the ultraviolet radiation tended to reduce the extent of this bleaching, possibly due to a competing reaction. The UV tends to remove the carbonyl group while the ionizing radiation causes a slight, though not spectrally selective, absorption. It would appear that the absorption spectrum of this polymer will depend to a large measure on the intensities of the ultraviolet and ionizing radiation. If this hypothesis is true, then one must know more about the flux of ionizing radiation in relation to ultraviolet before meaningful performance predictions can be made. This is, of course, significantly different from the Teflon data which showed that there was virtually no rate-dependence for that polymer. This difference in behavior is even more clearly seen when the combined proton/ultraviolet data are considered. The rate of ionizing radiation is a factor of 600 times as great as would be expected in space while the ultraviolet is only accelerated by a factor of 3. No bleaching is observed and the polymer becomes black (totally absorbing) in the short wavelength region almost immediately. This initial blackening results in a significant increase in solar absorptance which continues as irradiation is continued but at a much slower rate. In fact, after the initial period, the rate of degradation is not much greater than that observed for Teflon.

The question, however, arises that if the absorption band had been bleached prior to exposure to ionizing radiation, would the performance have been similar to that observed with Teflon? A non-spectrally selective absorption and linear rate of degradation rather than the behavior measured would make Butvar an excellent candidate for a series emittance coating. These questions obviously can only be answered by a much more extensive evaluation of Butvar than was conducted on this program.

APPENDIX A

ADHESIVE EVALUATION

The most probable means of utilizing series emittance coatings is in a tape configuration where a pressure-sensitive adhesive is applied to the metal surface of the film.

A brief examination of three candidate adhesives (SR 585, DC 281, SR 527) was conducted on this program. All three are pressure-sensitive silicone adhesives. SR 585 after spraying onto the metal foil and allowing for solvent evaporation can be used without any further treatment, while the other two require an elevated temperature exposure of 10 minutes at 150°C prior to use.

Test specimens consisting of aluminum foil 1 inch wide, 1 mil thick, and 6 inches long were prepared for evaluation. The samples were heated to 125°C for 24 hours. Subsequent to this exposure, the samples were placed in an all metal vacuum chamber where they were heated, one at a time, to 125°C at 10^{-5} torr for 24 hours. The chamber was arranged so that any outgassing products emanating from the adhesive would deposit on a sapphire window and/or onto aluminized collector plates. This apparatus was designed to measure the condensation of outgassing products in high vacuum and is described in detail in Ref. 6.

Infrared transmission measurements were made on the sapphire windows (3-6 microns) and reflection measurements on aluminized collector plates (3-20 microns) after they were exposed for 24 hours. No condensation products were detected on the windows or plates.

Peel strength was measured on identical samples before and after exposure to this environment and no significant changes were observed.

It appears from this cursory examination that the selection of adhesives should present no major obstacle in the utilization of series emittance coatings.

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